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Three manganese complexes of anionic N₄-donor Schiff-base macrocycles: monomeric Mn(II) and Mn(III), and dimeric Mn(IV)

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Dedicated to Emeritus Professor Richard Robson (University of Melbourne), an outstandingly innovative and intelligent scientist, and a true gentleman, whose seminal research contributions to macrocyclic chemistry and metal organic frameworks are internationally renowned.

Three manganese macrocyclic complexes of two anionic N₄-donor [1+1] Schiff-base macrocycles that differ in ring size (14 vs 16 membered), HL₂⁰ and HL₄⁰ (obtained from condensation of diphenylamine-2,2'-dicarboxaldehyde and either diethylenetriamine or dipropylenetriamine), are reported. Specifically, a pair of monomeric complexes MnHL₄₀(NCS)(H₂O) and [MnHL₄₀(NCS)]₂•0.5H₂O, plus a dimeric complex [MnHL₄₀L₄(O₂)(ClO₄)₂]•3DMF have been synthesised and characterised. Single crystal structure determinations on [MnHL₄₀(NCS)]₂•0.5H₂O and [MnHL₄₀L₄(O₂)(ClO₄)₂]•3DMF revealed octahedral manganese centres in both cases: N₄-coordinated Jahn-Teller distorted Mn(III) in the former and a pair of N₂O₂-coordinated Mn(IV) in the latter. UV-vis, IR and EPR spectroscopy as well as magnetic measurements are reported. These macrocyclic complexes feature a simple and original design, and could find future uses as models for manganese catalase or as building blocks for the assembly of larger supramolecular architectures.

Introduction

Macrocycles are polydentate ligands with the donor atoms either incorporated in, or less commonly attached to, a cyclic backbone.¹ Porphyrins, chlorins and corrins are classes of macrocycles naturally occurring, highly conjugated, tetrapyrrolic, N₄-donor macrocycles.² The complexes of all of these porphyrin-like N₄-donor macrocycles are biologically important molecules exhibiting a variety of critical functions, such as oxygen transport (haemoglobin: iron complex of porphyrin), photosynthesis (chlorophylls: magnesium complexes of chlorin) and formation of blood in our body (vitamin B₁₂: cobalt complex of corrin).³⁻⁵ Manganese ions are also involved in the active sites of a number of metalloenzymes that perform biological redox reactions.³⁻⁶ In these natural systems, the manganese ions cycle through various different oxidation states during the catalytic cycle. Manganese catalases, which are responsible for the disproportionation of two molecules of hydrogen peroxide into water and oxygen, possess a dinuclear, O-bridged, manganese active site which cycles between Mn(II)-₃ and Mn(II)-Mn(IV) during the catalytic cycle.⁷⁻⁸ This, and interest in the MnCa cluster in photosystem II which undergoes a cycle of four oxidation steps in order to catalyse the oxidation of two molecules of water into oxygen and protons,⁹⁻¹⁷ has led to di- and poly-nuclear manganese complexes in a range of oxidation states being studied as models for the active sites of these systems.¹⁸⁻²⁶ Macrocycles are a very useful ligand type for producing models of such biological active sites, not least as they provide a lot of control over the coordination site of the bound metal ion(s).²⁷ Interest in Schiff-base macrocycles in particular has remained high, and remains a particular strength in Australasia ever since the pioneering contributions to this field by Neil Curtis²⁸⁻²⁹ and Richard Robson.³⁰ In this paper we describe the synthesis and characterisation of three manganese complexes of a pair of N₄-donor [1+1] Schiff base macrocycles, differing only in ring size, developed previously in our group.³¹⁻³³ as we built on studies, published a decade earlier, by David Black.³⁴ Whilst these anionic macrocycles, (L⁴⁰) and (L₄⁰), share some similarities with the naturally occurring porphyrin and porphyrin-like macrocycles (above), in that they all provide an N₄-donor environment, herein they exhibit a significant difference: greater flexibility of coordination mode, as might be
expected given the far lower extent of conjugation. The results
manganese complexes, \( \text{Mn}^{II}L^1\text{Pr}(\text{NCS})(\text{H}_2\text{O}) \)
\( [\text{Mn}^{II}L^1\text{Pr}(\text{NCS})_2]·0.5\text{H}_2\text{O} \) and \( [\text{Mn}^{IV}L^2\text{Pr}(\text{O})_2]\)·\(3\text{DMF} \)
vary in oxidation states (+II, +III or +IV), ligand binding modes
(meridional or facial), and nuclearity (monomer or dimer).

**Results and Discussion**

The pair of monomeric complexes, \( \text{Mn}^{II}L^1\text{Pr}(\text{NCS})(\text{H}_2\text{O}) \)
\( [\text{Mn}^{II}L^1\text{Pr}(\text{NCS})_2]·0.5\text{H}_2\text{O} \), was synthesised in good yields
(78%) by the addition of one equivalent of \( \text{Mn}^{II}(\text{py})_4\text{(SCN)} \)
under an inert atmosphere, to a suspension of the appropriate
macrocycle in dry MeOH (Scheme 1). Simulation yielded
immediate colour change from pale orange to dark brown.
Note that in both cases the pyridine present in the manganese thiocyanate reagent, \( \text{Mn}^{II}(\text{py})_4\text{(SCN)} \),
expected to have deprotonated the macrocycle.

![Scheme 1. The synthetic route to the manganese Schiff-base macrocycle complexes reported herein: top \( \text{Mn}^{II}L^1\text{Pr}(\text{NCS})(\text{H}_2\text{O}) \), middle \( [\text{Mn}^{II}L^1\text{Pr}(\text{NCS})_2]·0.5\text{H}_2\text{O} \), bottom \( [\text{Mn}^{IV}L^2\text{Pr}(\text{O})_2]\)·\(3\text{DMF} \).](image)

After stirring under argon for 2 hours, the colour slowly changed
to dark brown for \( \text{Mn}^{II}L^1\text{Pr}(\text{NCS})(\text{H}_2\text{O}) \). In the case of \( [\text{Mn}^{II}L^1\text{Pr}(\text{NCS})_2]·0.5\text{H}_2\text{O} \), the reaction solution was opened
to air after stirring during 4 hours under Ar, which resulted in
immediate colour change from pale orange to dark brown. After
exposure to air for 3 hours with no obvious further colour
change, the \( \text{HL}^1\text{Pr} \) reaction solution was vapour diffused
diethyl ether, in air, giving \( \text{Mn}^{II}L^1\text{Pr}(\text{NCS})(\text{H}_2\text{O}) \) as a brown solid.
In the case of \( [\text{Mn}^{II}L^1\text{Pr}(\text{NCS})_2]·0.5\text{H}_2\text{O} \), a longer period
exposure to air, 7 days was found to be optimal to obtain the pure
manganese(III) complex, which conveniently precipitates on
a red solid. X-ray quality dark red blocks of \( [\text{Mn}^{III}L^1\text{Pr}(\text{NCS})_2] \)
were obtained by diethyl ether vapour diffusion into a MeOH
solution of the reaction solution in air. An attempted synthesis of
the manganese(III) complex of the \( \text{L}^2\text{Pr} \) macrocycle resulted in
the manganese(II) complex.

The third complex was formed by complexation of \( \text{HL}^2\text{Pr} \) with
\( \text{Mn}^{III}(\text{ClO}_4)_2·6\text{H}_2\text{O} \) and one equivalent of base (NEt) in air, in a
1:1 mixture of dichloromethane and methanol, followed by
diethyl ether vapour diffusion into the dark brown solution to
give a dark brown solid. Diethyl ether vapour diffusion into a
DMF solution of the sample, in air, gave a dark brown powder
along with dark brown needles of \( [\text{Mn}^{IV}L^2\text{Pr}(\text{O})_2]\)·\(3\text{DMF} \) suitable for an X-ray structure
determination. The tentative assignment of the manganese(IV)
oxidation state is based on the magnetic moment data and the
structure determination (see below).

The positive ion electrospray mass spectra of \( \text{Mn}^{II}L^1\text{Pr}(\text{NCS})(\text{H}_2\text{O}) \), \( [\text{Mn}^{III}L^1\text{Pr}(\text{NCS})_2]·0.5\text{H}_2\text{O} \) and the crystals
of \( [\text{Mn}^{IV}L^2\text{Pr}(\text{O})_2]\)·\(3\text{DMF} \) show a common peak, the
fragment \( [\text{Mn}(\text{L}^2\text{Pr})^\text{Pr}^\text{II}]^+ \), which is associated with the loss of an
additional proton and the perchlorate or thiocyanate co-
ligand. Importantly, the Mn(IV) dimer also shows a peak
corresponding to a \( [\text{Mn}L^2\text{Pr}(\text{O})_2]\text{(ClO}_4)_2 \) dimer fragment.

The infrared spectra of the three manganese complexes had
imine stretches in the range 1611-1628 cm\(^{-1}\). In the \( \text{L}^1\text{Pr} \)-
complexes the imine stretches (1624, 1628 cm\(^{-1}\)) occurred at
slightly lower energies than in the metal-free macrocycle \( \text{HL}^1\text{Pr} \)
(1629 cm\(^{-1}\)) whereas in the \( \text{L}^2\text{Pr} \)- complex the imine stretch
(1611 cm\(^{-1}\)) was at a significantly lower energy than in crude
metal-free \( \text{HL}^2\text{Pr} \) macrocycle (1628 cm\(^{-1}\) ), as observed in
previously reported complexes of \( \text{L}^2\text{Pr} \).\(^{32}\) The v(CN) stretch of
the thiocyanate ions in \( \text{Mn}^{II}L^1\text{Pr}(\text{NCS})(\text{H}_2\text{O}) \) and
\( [\text{Mn}^{III}L^1\text{Pr}(\text{NCS})_2]·0.5\text{H}_2\text{O} \) is observed at 2050 and 2039 cm\(^{-1}\),
respectively, and is consistent with terminal N-bound ligand
(literature range \( \geq 2050 \text{ cm}^{-1} \)),\(^{35}\) which was subsequently
confirmed by X-ray crystallography (see below). The Mn(IV)
dimer showed two bands at 1074 cm\(^{-1}\) and 621 cm\(^{-1}\), confirming
the presence of the perchlorate anion.

The room temperature magnetic moment of 6.07 \( \mu_\text{B} \)
\( \text{Mn}^{III}L^1\text{Pr}(\text{NCS})(\text{H}_2\text{O}) \) confirms a high-spin Mn(II) \( S = \frac{5}{2} \) central
ion. Its fluid solution EPR spectrum recorded at X-band
exhibited the characteristic six-lines from coupling of the
electron spin to the \( ^{55}\text{Mn} \) \( I = \frac{7}{2} \) (100% natural abundance)
nucleus (Figure S1). Simulation yielded \( g_{\text{iso}} = 2.0026 \) and a
hyperfine coupling constant of \( A_{\text{iso}} = 89 \times 10^{-4} \text{ cm}^{-1} \) typical for
Mn(II). The Mn(III) ion in \( \text{Mn}^{III}L^1\text{Pr}(\text{NCS})_2 \cdot 0.5\text{H}_2\text{O} \) is high-
spin as denoted by its temperature independent \( \mu_\text{eff} \) value of 4.91
\( \mu_\text{B} \) (50-300 K) for an \( S = 2 \) ground state (Figure S2). Below 50
K, \( \mu_\text{eff} \) decreases due to the influence of zero-field splitting.
The susceptibility has been successfully modelled with a sizeable \( D \)
\( = 6.5 \text{ cm}^{-1} \) at near full rhombicity, \( E/D = 0.029 \). These
parameters are consistent with Mn(II) \( S = 2 \) in such a ligand
field, and with being EPR silent at X-band.\(^{36,38}\) Full variable
temperature (VT) measurement conducted in the temperature
range 2–300 K for \( [\text{Mn}^{IV}L^2\text{Pr}(\text{O})_2]\text{(ClO}_4)_2·3\text{DMF} \) (Figure S3)
gave a \( \mu_\text{eff} \) value of 3.91 \( \mu_\text{B} \) per Mn, consistent with 3 upe
and hence Mn(IV). This \( \mu_\text{eff} \) value drops only very slowly as the
temperature is reduced, to a value of 2.74 \( \mu_\text{B} \), before dropping
rapidly thereafter. This profile is consistent with antiferromagnetic coupling.

161 X-ray Crystal Structures

162 Crystal structure determinations were carried out on [MnIIIPr(NCS)2] and [MnIVPL2(O)2](ClO4)2·3DMF.

163 Examination of these structures revealed that [MnIIIPr(NCS)2] is mononuclear with the manganese(III) ion in a Jahn–Teller distorted octahedral N6 donor environment whereas [MnIVPL2(O)2](ClO4)2·3DMF is dinuclear with the manganese(IV) ions also in an octahedral geometry.

164 Dark red blocks of [MnIIIPr(NCS)2] were obtained by diethyl ether vapour diffusion into a MeOH solution of the sample and the crystal structure determined (Figure 1).

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Figure 1. Perspective view of one of the two independent molecules of [MnIIIPr(NCS)2]. Non acidic hydrogen atoms omitted for clarity.

166

Table 1. Selected bond lengths (Å), angles (°) and other parameters in the two independent molecules of [MnIIIPr(NCS)2].

167

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn–Naque. Mn(1)–N(1) / Mn(2)–N(6)</td>
<td>1.922(7), 1.913(7)</td>
</tr>
<tr>
<td>Mn–Namine. Mn(1)–N(2) / Mn(2)–N(7)</td>
<td>2.031(7), 2.020(8)</td>
</tr>
<tr>
<td>Mn–Namine. Mn(1)–N(3) / Mn(2)–N(8)</td>
<td>2.087(7), 2.101(8)</td>
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<tr>
<td>Mn–Namine. Mn(1)–N(4) / Mn(2)–N(9)</td>
<td>2.015(7), 2.003(8)</td>
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<tr>
<td>Mn–NCS: Mn(1)–N(50)/Mn(2)–N(70)</td>
<td>2.217(7), 2.223(9)</td>
</tr>
<tr>
<td>Mn–NCS: Mn(1)–N(60)/Mn(2)–N(80)</td>
<td>2.203(7), 2.230(9)</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Bond Angle (°)</th>
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</tr>
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<tbody>
<tr>
<td>N(1)–Mn(1)–N(2) / N(6)–Mn(2)–N(9)</td>
<td>88.5(3), 89.0(3)</td>
</tr>
<tr>
<td>N(1)–Mn(1)–N(4) / N(6)–Mn(2)–N(7)</td>
<td>88.0(3), 88.4(3)</td>
</tr>
<tr>
<td>N(3)–Mn(1)–N(2) / N(8)–Mn(2)–N(7)</td>
<td>92.4(3), 91.2(3)</td>
</tr>
<tr>
<td>N(3)–Mn(1)–N(4) / N(8)–Mn(2)–N(9)</td>
<td>91.0(3), 91.4(3)</td>
</tr>
<tr>
<td>N(1)–Mn(1)–N(3) / N(6)–Mn(2)–N(8)</td>
<td>178.7(3), 178.8(3)</td>
</tr>
<tr>
<td>N(2)–Mn(1)–N(4) / N(9)–Mn(2)–N(7)</td>
<td>176.0(3), 173.4(3)</td>
</tr>
</tbody>
</table>

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<table>
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<tr>
<th>Pheny1 rings twist (°)</th>
<th>62.48, 60.55</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis N–Mn–N angles (°)</td>
<td>88.0–92.4, 88.4–91.4</td>
</tr>
<tr>
<td>trans N–Mn–N angles (°)</td>
<td>176.0–178.1, 177.4–178.0</td>
</tr>
<tr>
<td>Average Mn–N distance (Å)</td>
<td>2.014, 2.009</td>
</tr>
</tbody>
</table>

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The complex crystallises in the monoclinic space group P21/n. The monoanionic tetradentate macrocyclic ligand is bound to the equatorial plane of the metal centre through all four nitrogen atoms (one amine, one deprotonated amine and two imine nitrogen donors). In addition to the macrocycle, two axially coordinated (trans) isothiocyanate anions are also bound to the manganese(III) centre, forming an N6 coordination environment.

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There are two entire [MnIIIPr(NCS)2] complexes in the asymmetric unit. The Mn(2) complex has no disorder whereas in the Mn(1) complex both CS atoms of the NCS– anions and the four alkyl carbon atoms adjacent to the N(3) atom and the NH proton in the central part of the dipropylene trimine alkyl chain are disordered over two sites (occupancy of 0.75:0.25).

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The shortest Mn–N bond distance involves the deprotonated diphenylamine nitrogen atom, Mn–Naque [1.922(7), 1.913(7) Å], whereas the longest is the Mn–Namine bond [2.087(7), 2.101(8) Å]. The four crystallographically independent Mn–Namine bond lengths are equivalent within experimental error and are of intermediate lengths (average 2.017 Å; Table 1).

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A few dark brown needles of [MnIVPL2(O)2](ClO4)2·3DMF were obtained by diethyl ether vapour diffusion into a DMF solution of the sample, in air, and the crystal structure determined (Figure 2 and Table 2). The complex crystallises in the monoclinic space group P21/n with the entire complex in the asymmetric unit.

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Figure 2. Perspective view of the cation of [MnIVPL2(O)2](ClO4)2·3DMF. Hydrogen atoms, ClO4– anion and solvent of crystallisation omitted for clarity.

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The geometry around each manganese centre is approximately octahedral, the ligating atoms being two cis oxo bridges and the four nitrogen atoms (one amine, one deprotonated amine and two imine nitrogen donors) from the (LPr) macrocycle. This is the first observation of this tetradentate macrocycle binding in a capping not equatorial, mode (and hence the co-ligands occupying cis sites): all previous structurally characterised complexes feature an equatorial binding mode (with the co-ligand in trans sites). This 14-membered anionic N-donor macrocycle has similarities to the 16-membered porphyrins, but this binding mode highlights a key difference: significantly...
greater flexibility (due to much less conjugation) which enab
the capping binding mode observed here.

| Table 2. Comparison of selected bond lengths (Å), angles (°) and other parameters for [MnIII\textsuperscript{IV}\textsuperscript{3+}]L\textsuperscript{L2}(O\textsuperscript{2-})(ClO\textsubscript{4})\textsuperscript{3+}DMF. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Bond Length (Å) | Bond Angle (°)  |
| Mn(1)–O(1)      | 1.811(2)        | Mn(2)–O(1)      | 1.810(2)        | 1.823(2)        | 1.823(2)        | 1.859(2)        |
| Mn(1)–O(2)      | 1.819(3)        | Mn(2)–O(2)      | 1.822(2)        | 1.823(2)        | 1.823(2)        | 1.859(2)        |
| Mn(1)–N(1)      | 1.978(3)        | Mn(2)–N(21)     | 1.969(3)        | 1.990(3)        | 1.990(3)        | 2.019(3)        |
| Mn(1)–N(2)      | 2.004(3)        | Mn(2)–N(22)     | 1.990(3)        | 1.990(3)        | 1.990(3)        | 2.019(3)        |
| Mn(1)–N(3)      | 2.076(3)        | Mn(2)–N(23)     | 2.065(3)        | 2.065(3)        | 2.065(3)        | 2.086(3)        |
| Mn(1)–N(4)      | 2.010(3)        | Mn(2)–N(24)     | 2.011(3)        | 2.011(3)        | 2.011(3)        | 2.032(3)        |
| Mn(1)–Mn(2)     | 2.708(10)       |                  | 2.708(10)       | 2.708(10)       | 2.708(10)       | 2.708(10)       |
| Phenyl rings twist (°) | 37.85, 51.96 |
| Average Mn-N distance (Å) | 2.017, 2.009 |
| Average Mn-O distance (Å) | 1.815, 1.818 |

The assignment of the single atom bridges as µ-oxo rather than µ-hydroxo, hence also the manganese oxidation state, +IV not +III was made only after careful consideration of the manganese coordination sphere, hydrogen bonding to another molecule and CSD searches. No evidence of a proton was found near either oxo atom in the difference maps.

To further probe the assignment of manganese oxidation states in [Mn\textsuperscript{IV}\textsuperscript{3+}]L\textsuperscript{L2}(O\textsuperscript{2-})(ClO\textsubscript{4})\textsuperscript{3+}DMF, a comparison with related structures was conducted. A search of the CSD (vers. 5.39) for N\textsubscript{2} coordinated, bis-O (any type) bridged, dimanganese complexes resulted in 104 hits, of which only 74 involved 101, 102, 103, 104 bridging (the others mostly involved phenolate bridging). Narrowing the search to those structures where the oxidation states are clearly entered in the CSD provided useful oxidations which have been seen in some other bis(µ-oxo)-Mn\textsuperscript{V}\textsubscript{2} complexes with Mn--N\textsuperscript{equatorial} >> Mn--N\textsuperscript{axial}.

In summary, the comparisons of Mn--Mn separation, average Mn--O and Mn--N distances, and Mn--O--Mn angles in [Mn\textsuperscript{IV}\textsuperscript{3+}]L\textsuperscript{L2}(O\textsuperscript{2-})(ClO\textsubscript{4})\textsuperscript{3+}DMF with other complexes (Table 3) do not allow a definitive assignment of oxidation state, but overall it is most likely to be in the Mn\textsuperscript{IV}\textsuperscript{3+} oxidation state.

<table>
<thead>
<tr>
<th>Complex (CCDC code)</th>
<th>Mn\textsuperscript{III}</th>
<th>Mn\textsuperscript{IV}</th>
<th>Mn--O</th>
<th>Mn--N\textsubscript{eq}</th>
<th>Mn--N\textsubscript{ax}</th>
<th>Mn--O--Mn</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn\textsuperscript{III}\textsuperscript{IV} \textsubscript{2}</td>
<td>(KAWLID)</td>
<td>2.676(3)</td>
<td>2.184-1.863</td>
<td>2.406-2.468</td>
<td>2.099-2.121</td>
<td>92.1(4)-94.5(4)</td>
<td>[**]</td>
</tr>
<tr>
<td>Mn\textsuperscript{III}\textsuperscript{IV}</td>
<td>(SEIXUA)</td>
<td>2.741(1)</td>
<td>1.854-1.867</td>
<td>2.336-2.362</td>
<td>2.116-2.129</td>
<td>97.7</td>
<td>[**]</td>
</tr>
<tr>
<td>Mn\textsuperscript{III}\textsuperscript{IV}</td>
<td>(FEBKOM)</td>
<td>2.748(2)</td>
<td>1.797-1.805</td>
<td>1.999-2.020</td>
<td>2.069-2.087</td>
<td>99.5(2)</td>
<td>[**]</td>
</tr>
<tr>
<td>[Mn\textsuperscript{III}\textsuperscript{IV}\textsubscript{L2}(O\textsuperscript{2-})(ClO\textsubscript{4})\textsuperscript{3+}DMF</td>
<td>2.708(10)</td>
<td>1.810-1.826</td>
<td>1.963-2.076</td>
<td>1.990-2.013</td>
<td>96.0(1)-96.8(1)</td>
<td>this work</td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

Three manganese complexes, $\text{Mn}^{III}{\text{L}^\text{III}}(\text{NCS})(\text{H}_2\text{O})$ (H3), $\text{Mn}^{III}{\text{L}^\text{IV}}(\text{NCS})_2$ (H2) and $\text{Mn}^{IV}{\text{L}^\text{IV}}(\text{O})_2(\text{ClO}_4)_2$ (H1), were prepared by deprotonation and metallation of the respective metal-free Schiff-base macrocycles, $\text{HL}^\text{III}$ and crude $\text{HL}^\text{IV}$. These anionic N$_2$-donor macrocycles have similarities with the analogous N$_2$-donor porphyrins, but also significant differences: hence their far greater flexibility, due to a much lower degree of conjugation, is demonstrated in the binding modes adopted by either meridional (equatorial plane square; trans co-ligands) or facial (capping; cis co-ligands). Also reported here are the first examples of these diphenylamine-2,2'-dicarboxaldehyde-based macrocycles facilitating access to 3D complexes in a wider range of oxidation states, +II, +III and +IV: all previous complexes having been isolated only in the +II oxidation state. The mononuclear complexes produced are of interest as building blocks for larger supramolecular architectures. Our current efforts are focussed on refining the macrocycle design further, in particular aiming to increase the denticity and to include surface anchoring groups.

Experimental

Magnetic data for $\text{Mn}^{III}{\text{L}^\text{III}}(\text{NCS})(\text{H}_2\text{O})$ was recorded at 300 K using a Quantum Design Physical Property Measurements System (PPMS) equipped with a vibrating sample magnetometer at 1 T. Variable temperature (2 – 300 K) magnetic susceptibility data for [Mn$^{III}{\text{L}^\text{IV}}(\text{NCS})_2$]•0.5H$_2$O were recorded in a 1 T magnetic field on a SQUID magnetometer (MPMS, Quantum Design). All magnetic data were corrected for diamagnetic contributions using Pascal’s constants. X-band EPR spectra of $\text{Mn}^{III}{\text{L}^\text{III}}(\text{NCS})(\text{H}_2\text{O})$ were collected on a Bruker EMX Micro spectrometer equipped with a ‘premium-X’ microwave bridge at 9.18 GHz. The structures were simulated using Xsophe. Elemental analyses were carried out by the Campbell Microanalytical Laboratory at the University of Otago.

MoH and DMF were HPLC grade, whereas DCM was reagent grade and used without purification. $\text{Mn}^{III}(\text{py})_2(\text{SCN})_2$ was used as received and the $\text{HL}^\text{III}$ macrocycle$^{11}$ was prepared as previously reported, but in the case of the $\text{HL}^\text{IV}$ macrocycle, rather than using the literature synthesis,$^{32}$ a crude sample of macrocycle was instead prepared without added acid (details below) and utilised without further purification.

$\text{Mn}^{III}{\text{L}^\text{III}}(\text{NCS})(\text{H}_2\text{O})$: Under an Ar atmosphere, to a bright yellow suspension of the macrocycle $\text{HL}^\text{III}$ (45.1 mg, 0.154 mmol) in methanol (30 mL) was added Mn$^{III}(\text{py})_2(\text{SCN})_2$ (75.3 mg, 0.352 mmol) as a solution in methanol (3 mL) resulting in a dark brown solid. After exposure to air for 7 days a dark red-brown precipitate was observed. The resulting dark red-brown solid was collected by filtration and dried in vacuo (185 mg, 78%). (Found: C, 53.18; H, 4.76; N, 16.73; S, 12.42%. Calc. for [C$_{23}$H$_{39}$N$_5$Mn$_2$O$_5$H$_2$O] (499.53 g mol$^{-1}$): C, 52.90; H, 4.84; N, 16.82; S, 12.84%). IR (ATR): $\nu$/cm$^{-1}$ = 3393, 3235, 2948, 2039, 1611, 1555, 1541, 1456, 1434, 1399, 1353, 1298, 1248, 1229, 1204, 1156, 1139, 1127, 1110, 1087, 1071, 1057, 1039, 989, 976, 954, 940, 886, 857, 782, 756, 734, 641, 606, 591, 548, 468, 448, 434, 409. ESI(+) MS (m/z) (MeCN): [Mn$^{III}{\text{L}^\text{III}}(\text{py})_2(\text{SCN})_2$]$^+$ expected 373.1185, found 373.1219. $\mu_{\text{eff}}$ (SQUID at 300 K) = 4.91 $\mu_B$. UV-vis (MeCN): $\lambda_{\text{max}}$/nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$) = 315 (10884), 478 (5093), 550 (1472), 872 (309). $\lambda_{\text{max}}$(MeCN) = 36 $\Omega$ cm$^{-1}$ mol$^{-1}$. X-ray quality crystals were grown by slow evaporation of the reaction solution, giving red blocks of [Mn$^{III}{\text{L}^\text{III}}(\text{NCS})_2$].

$\text{Mn}^{IV}{\text{L}^\text{IV}}(\text{O})_2(\text{ClO}_4)_2$: In vacuo, to a bright yellow solution of $\text{HL}^\text{IV}$ (90.4 mg, 0.309 mmol) in a 1:1 mixture of methanol and dichloromethane (40 mL) was added manganese(II) perchlorate hexahydrate (112.0 mg, 0.309 mmol) as a solution in methanol (3 mL) resulting in a dark brown solution. A solution of triethylamine (31.1 mg, 0.309 mmol) was added resulting in no further colour change. This dark brown solution was stirred at RT overnight and concentrated to 20 mL by blowing compressed air over it and subjected to diethyl ether vapour diffusion. The dark brown solid was collected, dried in vacuo, then left in air (65 mg, 21%). (Found: C, 44.12; H, 4.24; N, 10.95%. Calc. for [C$_{31}$H$_{51}$N$_5$O$_7$Cl$_2$Mn$_2$H$_2$O$_5$] (988.38 g mol$^{-1}$): C, 43.75; H, 4.61; N, 11.34%. IR (ATR): $\nu$/cm$^{-1}$ = 3504, 3293, 2946, 1628, 1596, 1559, 1541, 1458, 1436, 1395, 1281, 1195, 1163, 1084, 972, 912, 875, 852, 810, 755, 649, 621, 593, 562, 538, 492, 457. ESI(+) MS (m/z) (MeCN): [Mn$^{IV}{\text{L}^\text{IV}}(\text{O})_2(\text{ClO}_4)_2$]$^+$ expected 454.0906, found 454.0906 (PPMS at 300 K) = 3.91 $\mu_B$. UV-vis (MeCN): $\lambda_{\text{max}}$/nm (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$) = 374 (8222), 485 (3529). A few single crystals, suitable for an X-ray structure determination, were obtained by diethyl ether vapour diffusion into a DMF solution of the sample, giving dark brown needles of [Mn$^{IV}{\text{L}^\text{IV}}(\text{O})_2(\text{ClO}_4)_2$]$^+$3DMF.

X-ray Crystallography

Data were collected on a Bruker Kappa Apex II area detector diffractometer at 89-90 K using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Both data sets (Tables S1 and S2, S1) were absorption corrected using SCALE. The structures were
solved using SHELXS-97 and refined against \( F^2 \) using all data.

by full-matrix least-squares techniques with SHELXL-97.

non-hydrogen atoms were modelled anisotropically except where noted. Hydrogen atoms were attached at calculated positions and rode on the atoms to which they are attached except where noted. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (Entry numbers CCDC 1913017-1913018).

[2] Mn\(^{III}\)P\(^{+}(\text{NCS})3\): The asymmetric unit contains 2 [Mn\(^{III}\)P\(^{+}(\text{NCS})3\)] complexes. The Mn(2) complex has disorder, whereas in the Mn(1) complex both the thiocyanate

ions have the CS atoms disordered over two sites with 0.75:0.25 occupancy whilst the N atom is full occupancy. 0.25 alkyl carbon atoms adjacent to the N atoms in the dipropylene triamine chain and the NH proton are disordered with 0.75:0.25 occupancy. The NH and the central C in each propylene chain are full occupancy. All non-hydrogen atoms were refined anisotropically except for the 0.25 and 0.75 occupancy C and S atoms of the thiocyanate anion which were left isotropic.

[3] Mn\(^{III}\)Et\(^{2+}\)(O\(2\))\(Cl\(O\)\(2\))\(3\)DMF: The asymmetric unit comprises the entire macroyclic dimeric complex, two perchlorate anions and three DMF molecules of solvation. No disorder was present in the complex. One of the perchlorate ions was disordered over two sites with 0.8:0.2 occupancy. One of the DMF molecules was disordered over two sites with 0.7:0.3 occupancy. All hydrogen atoms were refined anisotropically except for the 0.3 occupancy perchlorate ion, C125, O25, O26, O27.

O28. The 0.3 occupancy DMF atoms, C75, O75, N75, C76, C77 were also refined isotropically.

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Conflicts of interest

There are no conflicts to declare.

References


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Monomeric and oxo-bridged dimeric manganese complexes of two flexible, anionic, [1+1] macrocycles, derived from diphenylamine-2,2'-dicarboxaldehyde and either diethyl- or dipropyl-enetriamine, are reported: both facial and meridional binding modes are observed.